

CHLORINE IN FIVE ILLINOIS COALS AND THREE BRITISH COALS:
AN X-RAY ABSORPTION NEAR-EDGE STRUCTURE (XANES)
SPECTROSCOPY INVESTIGATION.

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ABSTRACT

The chlorine x-ray absorption near-edge structure (XANES) spectra of five Illinois coals and three British coals, and two series of char samples were examined. The char samples were prepared by stepwise heating one Illinois and one British coal in air at temperatures from 200 to 650°C. The chlorine XANES spectra for all the coals are similar and chloride anion was determined to be the predominant form of chlorine. The identity of the positive counter ions with which the chlorine anions are associated in the coals could not be unambiguously determined from XANES spectra. Nevertheless, the XANES spectra of the raw coal and its partially combusted char samples show significant changes in the form (and concentration) of chlorine with increasing char preparation temperature. The appearance of NaCl was observed in the chars from the British sample between 200 to 350°C but was not observed in the chars from the Illinois sample. The appearance of sodium chloride in British chars and not Illinois chars may indicate an isolated incidence due to dehydration and to the high sodium content of these coals, but it could also imply that in the British coal sodium cations are paired with chloride anions and this sodium could be associated with the sodium sulfate mechanism of boiler corrosion.

INTRODUCTION AND BACKGROUND

The total Cl content in coal has been used in Great Britain to predict the boiler corrosivity of a coal. It has been reported that British coals with more than 0.3% Cl are not recommended for pulverized-coal-fired boilers.^{1,2} However, a recent survey conducted through a joint effort of the Electric Power Research Institute and the Illinois Clean Coal Institute indicates that many midwestern United States utilities have decades of experience burning high-Cl Illinois coals in a large variety of boiler equipment with no reported Cl-related fireside corrosion problems.³ This suggests that the extent of boiler corrosion may not be directly related to the amount of Cl in the coal but to how the Cl occurs in the coal or to other factors such as the alkali and sulfur content of the coal, the type of boiler in which the coals were burned, and boiler operating parameters.⁴

If the nature of the Cl in coals with different corrosion potentials varies, then determination of how the Cl occurs in coals may provide a method to assess a coal's boiler corrosion potential. The current American Society for Testing and Materials (ASTM) standard method can determine the total chlorine content, but not the forms of chlorine in coal⁵. In many previous attempts at determining the forms of chlorine in coals, indirect methods were used, and some mixed results were reported. For example, Hamling and Kaegi⁶ stated that chlorine in coal samples from one of the high-chlorine Illinois mines was predominantly in the form of organic chloride(s), and the organically associated chlorine does not apparently contribute to boiler corrosion and fouling problems. Chou⁷ suggested that chlorine in coals occurs in two major forms: chloride anions dissolved in the pore water of coal, and chloride anions adsorbed on the inner surfaces of the micropores in macerals (organic fraction of the coal). It is clearly desirable to generate representative data with a more direct method of determination. Huggins and Huffman⁸ recently used K-edge X-ray absorption fine structures (XAFS) spectroscopy to examine the occurrence of chlorine in coals from various locations worldwide. This nondestructive technique was applied in this study to directly examine five Illinois coals and three British coals and chars produced from the coals by stepwise heating under air.

EXPERIMENTAL PROCEDURES

Samples - Five Illinois coals, representing five specific geological locations⁹ in Illinois, and three coals previously obtained from Great Britain were analyzed for chlorine by XANES. Data on chlorine and ash composition of the coals are listed in Table 1. Illinois coals have

much higher moisture contents than the British coals. Two of the three British coals have high ash contents. Among these coals, the two high ash content British coals also contain the highest sodium and potassium content.

Char preparation - Partially combusted coal samples (chars) were prepared from two coals, an Illinois coal (C-32795) and a British coal (C-32500). The coal sample was placed in a constant temperature zone of a Lindberg tube furnace. Under a flow of air, the furnace temperature was increased from room temperature to 200°C and remained at 200°C for 30 minutes before the first sample was collected. After the first sample was taken out, the temperature was increased to 250°C and held at 250°C for 30 minutes in order for the second sample to be collected. This stepwise heating was continued and a sample was collected at each 50°C interval until the final temperature of 1000°C was reached. These partially combusted samples were submitted to the University of Kentucky for XANES analysis.

XANES analysis - Chlorine XAFS spectra were obtained at beam-line X19A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The spectra were obtained from the samples as-received by suspending them in the monochromatic X-ray beam in ultrathin (6 μm) polypropylene baggies. The chlorine XAFS spectra were collected in fluorescence geometry using a Lytle-type fluorescent detector with nitrogen as the ionization gas and helium in the sample chamber. The beam-line was operated in the focussed spot mode, although the spot was de-focussed somewhat in order to obtain a better sampling of the coal and char samples. Each spectrum consisted of about 500 points collected at energies between about 50 eV below the chlorine edge (2825 eV) to about 300 eV above the edge. Dilute samples of sodium chloride in boric acid were used as the primary standard for the chlorine edges. The principal peak position of the derivative XANES spectrum of NaCl was defined as the zero point of energy for the purpose of calibrating the chlorine XANES spectra. All spectra were collected and stored in a MicroVAX computer at NSLS and were transferred electronically to a similar computer at the University of Kentucky for analysis.

The chlorine spectra were first calibrated with respect to the primary standard (NaCl), then normalized to the edge step, corrected for background slope above and below the edge, and finally divided into separate XANES and extended X-ray absorption fine structure (EXAFS) regions. Analysis of the EXAFS regions of these spectra is generally not very informative, so that the data reported here comes from only the XANES region, that is, the structure within ± 50 eV of the chlorine K absorption edge.

RESULTS AND DISCUSSIONS

Variation of forms of chlorine in coals - Based on the XANES spectra of standard compounds⁸, a strong broad peak at about 1 eV followed by a much weaker, broad peak at about 20 eV is indicative of an ionic form of chlorine. The chlorine XANES spectra of the Illinois coals and the British coals are shown in Figures 1 and 2, respectively. The spectra of the Illinois coals and those of the British coals show a predominant form of chlorine as chloride anions. These anions may be in solution and have significant interaction with maceral surfaces presumably via ionic functional groups, such as quaternary amines or oxygen functional groups anchored via cations. The identity of these positive counter ions with which the chlorine anions are associated in the coals could not be unambiguously determined from XANES spectra. Nevertheless, the appearance of a sharp peak at 12.5 eV is indicative of the crystalline form of NaCl which is observed only in the spectrum of a British coal (C-33499). The ash composition of the coals indicated that this British coal is one of the coals which have high ash and high sodium contents.

Variation of forms and concentration of chlorine during stepwise heating under air - A procedure for the quantification of different forms of chlorine, similar to that done for sulfur¹⁰, has not been established because most coals appear to have only one major form of chlorine, chloride anion. In this study, a separate set of experiment, using stepwise heating of one British coal (C-32500) and one Illinois coal (C-32795) under air, was conducted to attempt to remove the more volatile chlorine step by step from the less volatile chlorine and examine the residues by XANES. The XANES analysis on the changes, if any, of the forms of chlorine in chars during stepwise heating may help in understanding the nature of chlorine in these coals. The XANES spectra of the Illinois and the British coal and their partially combusted char samples were compared, as shown in Figure 3. The XANES spectra show significant changes in the form of chlorine (and concentration) with increasing char preparation temperature. In addition, there are differences between the variation of chlorine in the British coal compared to that in the

Illinois coal. A small peak at about 12.5 eV, diagnostic of the presence of NaCl, is apparent in the spectra of the chars formed at 200 to 350°C from the British coal. This feature is absent from the spectra of chars from the Illinois coal. The ash composition of these coal indicated that the British coal (C-32500) used has high ash and high sodium contents.

Above 350°C, the spectra of chars from both coals show a prominent sharp peak at about -1 eV that dominates the spectra in the range 400 - 600°C. Above 600°C, the spectra degrade in quality, as virtually all of the chlorine has been evolved from the samples. The peak position and shape of the spectra for the chars prepared at 400°C are similar to those noted for chlorine in organic (aromatic) compounds⁸. However, other less similar chlorine forms (hypochlorite, e.g. NaOCl) could be possible. The possible presence of organic chlorine in these chars raises some interesting speculations as to its possible origin. Alternative possibilities are: (i) it was present in the coal originally, but at such a low level (<10% of the total chlorine) that it did not register in the Cl XANES spectrum of the coal until the more volatile forms of chlorine had been evolved during low-temperature char preparation; or (ii) it was formed by reaction between the char and HCl evolved during char preparation. This phenomenon, the appearance of "organic" chloride, was not seen in a previous investigation⁸, which was done by *in situ* heating under helium followed by XANES Cl analysis. In that study, however, the heating temperature was low, reaching only 350°C.

The chlorine content in the chars was estimated using a parameter known as step-height in the analysis of the chlorine XANES spectra. The results (Figure 4) showed that both coals experienced a large decrease in chlorine content at early stages of heating over the temperature range 250 to 400°C. The decrease of the remaining chlorine content in chars during further heating from 400°C to 600°C was very limited. In comparison with a previous study by Liu¹¹ in which chlorine evolution was based on HCl gas analysis, this study measured the chlorine content of the chars. In that study, the differences in chlorine evolution as a function of temperature between Illinois and British coals when heated under air were observed using a temperature-programmed thermogravimetric analyzer equipped with Fourier transform infrared spectrometry (TGA-FTIR). When comparing these two results, it should be noted the experiments in the two studies were conducted under different conditions. For example, the samples in this study during stepwise heating were heated much more slowly and at a longer residence time, which may have allowed more chlorine in the Illinois coals to be evolved at lower temperatures as compared with the TGA-FTIR analysis.

SUMMARY AND CONCLUSIONS

The data based on X-ray absorption near edge spectrum (XANES) analysis indicate that, in general, chlorine in coal mainly occurs in an ionic form. To balance the negative charge of these chloride anions, the occurrence of sodium and other cations, such as amino functional group, in the pore water of the coal are important. The identity of the positive counter ions with which the chlorine anions are associated in the coals could not be unambiguously determined from XANES spectra. Nevertheless, the current XANES data clearly indicated the appearance of NaCl in a British coal and in chars formed at 200 to 350°C from another British coal. The appearance of sodium chloride in the British char and not in the Illinois char may indicate an isolated incidence due to the dehydration of the coal sample and to the high sodium concentration of the coal samples, but it could also imply that in the British coal sodium cations are paired with chloride anions and this sodium could be associated with the sodium sulfate mechanism of boiler corrosion during coal combustion. Further investigation using *in situ* techniques to determine volatile alkali metals and chlorine-containing compounds produced during coal combustion may shed light on this speculation.

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Table 1. Ash composition and chlorine content in coals

Coal sample	Moisture	*Ash	*Na ₂ O	*K ₂ O	*Cl
Illinois coals					
C-32783	15.22	12.86	0.20	0.21	0.16
C-32779	12.62	9.63	0.14	0.20	0.08
C-32795	9.42	5.76	0.14	0.14	0.45
C-32661	6.79	8.17	0.07	0.20	0.26
C-32662	7.99	7.00	0.08	0.21	0.35
British coals					
C-33499	4.55	14.79	0.31	0.48	0.61
C-33500	4.16	22.24	0.31	0.89	0.43
C-33502	3.21	3.13	0.10	0.02	0.81

*% moisture free basis; Data on Illinois coals were provided by Dr. Ilham Demir of the ISGS.

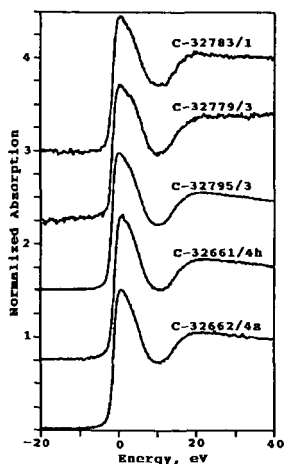


Figure 1: XANES spectra of the five Illinois coals and their specific geographic locations.

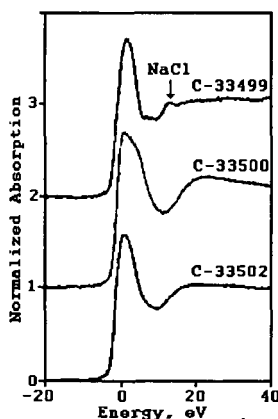


Figure 2: XANES spectra of the British coals.

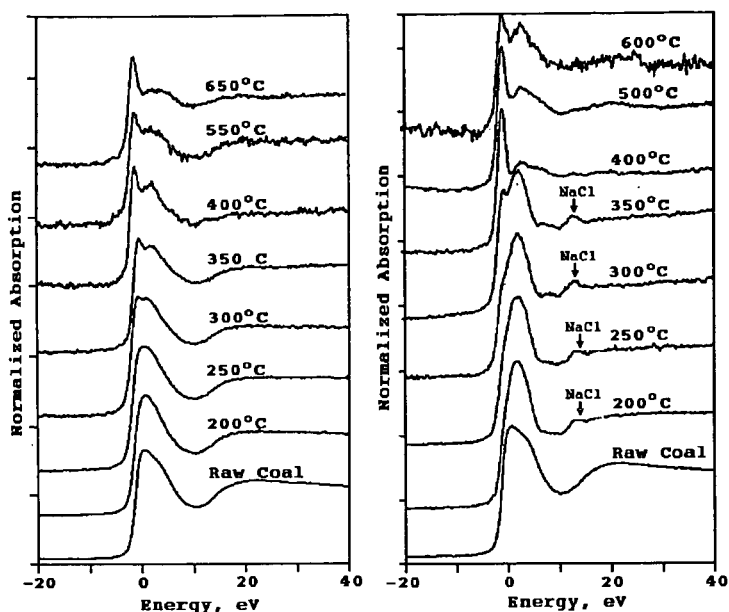


Figure 3: XANES spectra of one Illinois (C-32795, left) and one British (C-33500, right) coal and chars from step-wise heating under air.

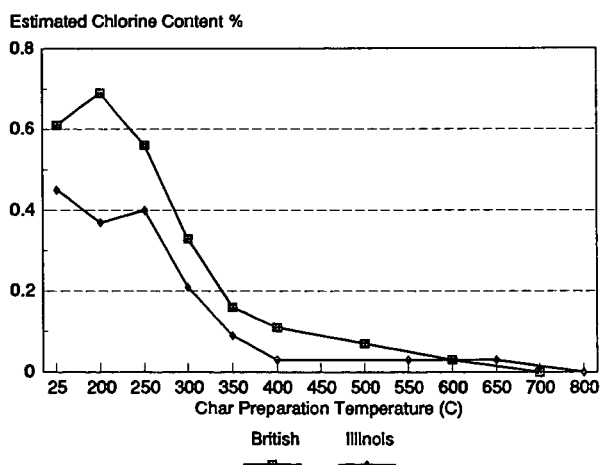


Figure 4: Comparing chlorine content in chars produced from stepwise heating of a British coal (C-32500) and an Illinois coal (C-32795) under air.